Dielectric Anomaly of Ammonium Sulfate at Its Transition Temperature

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Synopsis

Dielectric anomaly accompanied by a phase transition of the single crystal of ammonium sulfate was observed at audio and radio frequencies. It was found that a sharp peak appeared in a-axial direction and kinks appeared in b- and c-axial directions and that the transition temperature was −36°C on cooling and −29°C on warming.

The dielectric constants at room temperature were determined to be 8.0, 7.45 and 6.7 along a-, b- and c-axial directions, respectively. They are independent of frequency between 10 to 10^5 kc/sec.

It was also found that the transition temperature of pressed polycrystalline powder specimen was about −53°C, which was much lower than that of single crystal.

I. Introduction

Phase transition phenomena have been observed in many ammonium salts. Of these, several experimental results have been reported about the phase transition of ammonium sulfate. Hettner and Simon(1) measured the infrared transmission of the thin crystal of ammonium sulfate and found the anomaly at around −40°C. According to Pohlman's result(2) of the transmission study, however, the transition temperature was about −48°C. Grenshaw and Ritter(3) observed the anomaly of specific heat of this compound at −50.7°C. Three experimental results have hitherto been reported on the dielectric anomaly accompanied by this phase transition, namely, a sharp peak of λ-type observed by Guillien(4) at −53.4°C at the wavelength of 2700 m, a peak, but of different type, observed by Freymann(5) at −52°C at 9560 mc/sec, and a broad peak ranging from about −80°C to −35°C with the maximum at about −40°C found by Bayley(6) at 3 kc/sec. These results were obtained from the experiments made with the crystalline powder sample.

In this paper experimental results are described of the anomaly in dielectric constant measured along the three axial directions of the single crystal of ammonium sulfate at radio and audio frequencies.

II. Experimental apparatus

Measurements were made at radio (up to 40 mc/sec) and audio (down to 10

* The paper was reported in some abridgement to J. Chem. Phys., **22** (1954), 756.

(1) G. Hettner and F. Simon, Z. phys. Chem. **B 1** (1928), 293.
(2) R. Pohlman, Z. Phys. **79** (1932), 394.
(3) J. L. Grenshaw and I. Ritter, Z. phys. Chem. **B 16** (1932), 143.
(4) R. Guillien, Compt. rend. **208** (1939), 980.
(5) M. Freymann, Compt. rend. **233** (1951), 1449.
(6) S. T. Bayley, Trans. Farad. Soc. **47** (1951), 518.

kc/sec) frequencies. Dielectric constant and loss factor at audio frequencies were measured by the low frequency bridge (Fig. 1) which had been improved from an ordinary Schering bridge by Hall[7] for eliminating the effect of stray capacities between the test specimen and earth. Capacitance bridge made by General Radio Co. (type 716-C) was also used.

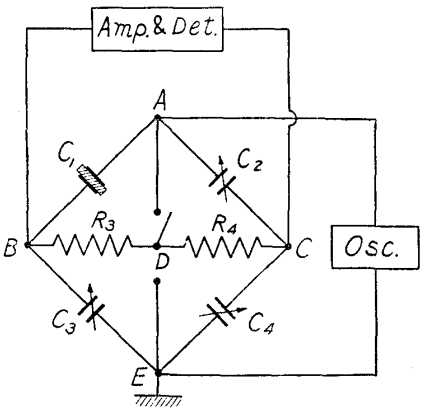

Fig. 1. Modified Schering bridge for low frequency measurement.

For radio frequency measurement, two-step beat-method (Fig. 2) was used, in which change in capacity of unknown specimen was compensated by the adjustment of the variable condenser connected parallel to the former so as to produce the zero beat figure on the cathode-ray tube, the amount of adjustment being the measure of the dielectric constant. For each measurements, unknown capacity was compared with the standard variable condenser, as shown in Fig. 2, so as to eliminate the zero shift of generating frequency caused by the supply voltage fluctuation or by the time change in valve characteristics.

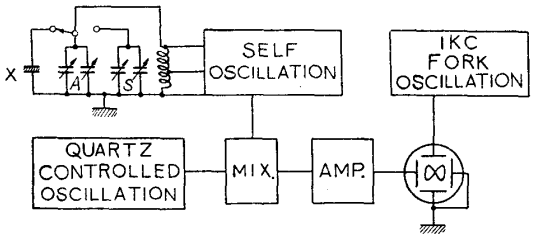

Fig. 2. Block diagram of the apparatus for the radio frequency measurement by two-step beat-method.
X: Specimen, S: Standard condenser
A: Auxiliary condenser

For an accurate determination of the dielectric constant of ammonium sulfate at room temperature, the electrode shown in Fig. 3 was used. The difference of the standard variable condenser, $C_x - C_0$, in Fig. 2 was measured with and without inserting the specimen. Then the dielectric constant, ε, is

$$\varepsilon = 1 + \frac{4\pi d}{S}(C_x - C_0),$$

where S and d are the area and gap of the electrodes, respectively. The gap can be measured by the screw microscope to the accuracy of 0.01 mm. The details of the procedure in measurement and the calibration of the standard variable condenser were already described.[8]

In the determination of the temperature dependence of the dielectric constants, only the differences from the values at room temperature were determined, and the true dielectric constant was calculated by the following equation:

$$\Delta\varepsilon = \frac{4\pi d}{S}\Delta C,$$

where ΔC and $\Delta\varepsilon$ are the differences of capacity and the corresponding dielectric constant from the room temperature values. Fig. 4 shows the sample condenser

(7) H. C. Hall, J. Sci. Instr. **29** (1952), 224. See also K. Kamiyoshi and T. Odake, Sci. Rep. RITU **A 5** (1953), 271.
(8) K. Kamiyoshi, Sci. Rep. RITU **A 1** (1949), 305.

for the determination of the temperature variation of the dielectric constant. The electrodes are 18 mm in diameter, tin foils were inserted in between the electrodes

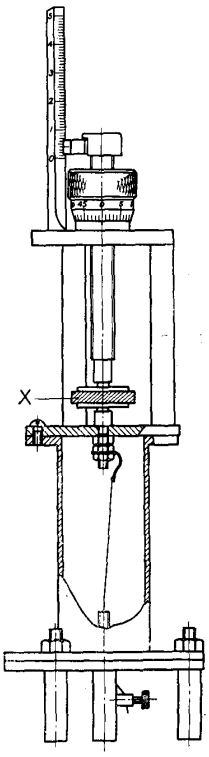

Fig. 3. Sample electrodes for an accurate determination of the dielectric constant at room temperature.
X : Specimen.

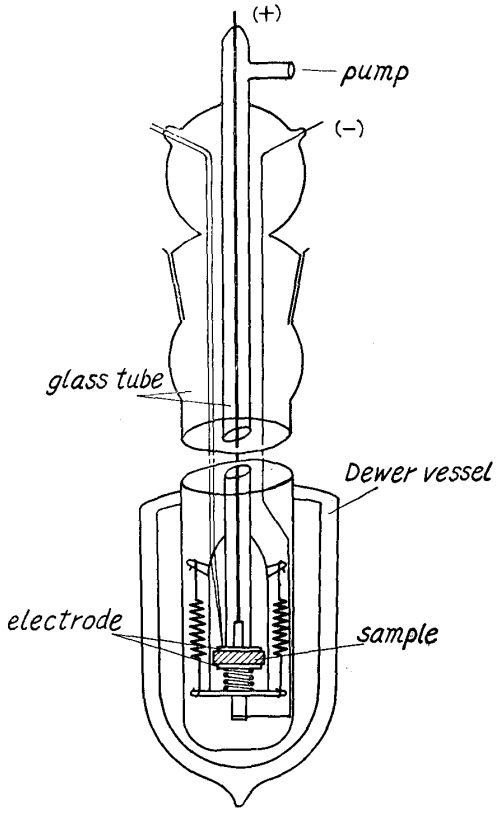

Fig. 4. Sample electrodes in vacuum vessel for the low and high temperature measurements.

and the sample for the elimination of air gaps. The glass vessel was evacuated to less than 10^{-4} mmHg during the course of experiments. A copper-constantan junction was used for temperature measurements.

III. Preparation of samples

Single crystals used in this experiments were grown from aqueous solution. First the cooling method was employed. The aqueous solution of ammonium sulfate (300 gr in 400 cc water) was cooled from about 50°C to room temperature at the rate of about 1−1.3°C per day. Crystal growth began at about 40°C. Crystal seed, a few millimeters in size, was put on the glass plate in the solution. The capacity of the solution vessel was about 12 cm in diameter and 15 cm in depth. Temperature control was performed by the water bath of about 30 cm in diameter with a toluol-mercury switch, which is sensitive to the fluctuation of 0.1°C.

Later the constant-temperature method was employed. The temperature of the solution was kept constant at 25°C and the water in the solution was evapolated out by throttling the cover glass plate. Photo 1 is one of the single crystals grown by this method (for about 30 days).

For the determination of crystal axes, the following method was used. According

to Tutton[9], the ammonium sulfate crystal is the orthorhombic system with the length of three axes:

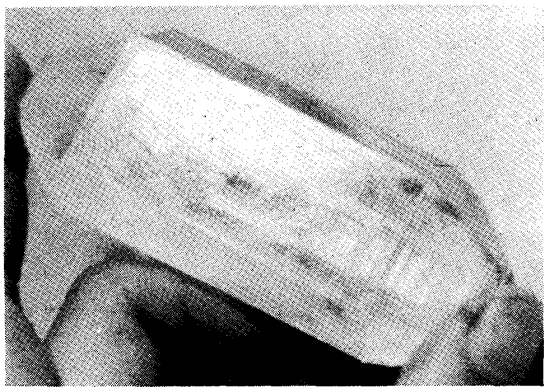

Photo. 1. Single crystal of ammonium sulfate.3/4 act. Size.

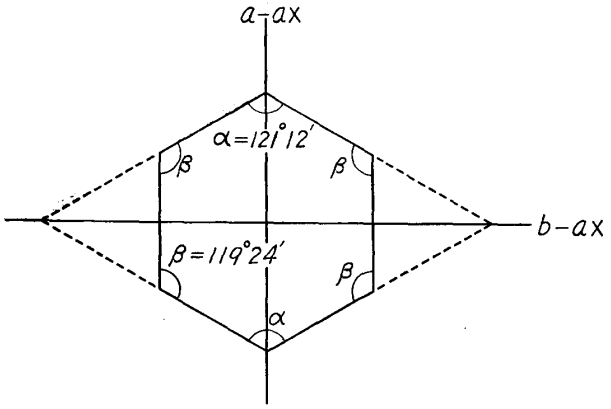

Fig. 5. The figure of the section cut perpendicular to c-axis of the crystal of ammonium sulfate.

$$a=5.951,\quad b=10.560,\quad c=7.729\text{Å}.$$

The figure of the section cut perpendicular to c-axis of this crystal is a hexagon as shown in Fig. 5, and

$$\alpha=121°12'\qquad \beta=119°24'.$$

The crystal grows most easily along c-axis, so it is usually long in this direction. Therefore, we can easily discriminate the direction of c-axis from others. We can determine a- and b-axes by measuring the angle of the hexagon when the crystal is cut perpendicular to c-axis.

The measurement of the angle was made by the Toolmaker's Microscope made by Zeiss Co. (accuracy 1′ by direct reading).

For the measurement of the dielectric constant, three slices, perpendicular to three axes respectively, were cut from one single crystal. Care had to be taken when cutting them perpendicular to a- and b-axes because of the cleavage.

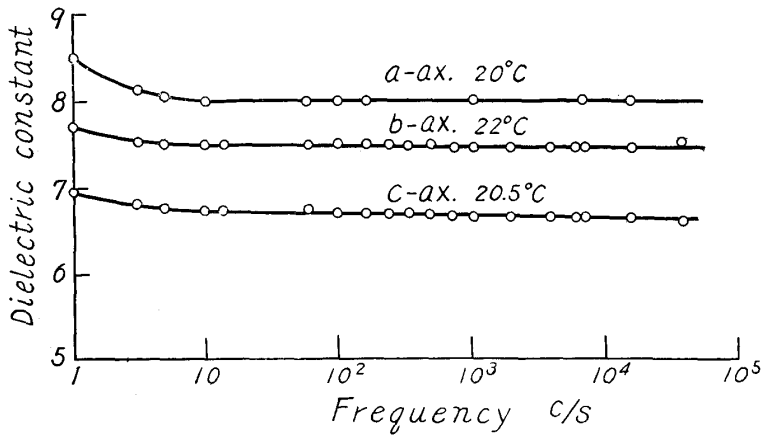

Fig. 6. Frequency dependence of the dielectric constants in three axial directions of ammonium sulfate at room temperature.

IV. Experimental results

Accurate determinations of the dielectric constant of ammonium sulfate were performed at room temperature by the method described in section III. Fig. 6 shows the frequency dependence of the dielectric constants along three axial directions. The dielectric constants are 8.0, 7.45 and 6.7 along a-, b- and c-axial directions, respectively. It

(9) A. E. H. Tutton, Phil. Mag. 8 (1929), 195. See also R. W. G. Wyckoff, *The Structure of Crystals* (The Chemical Catalog Co., Inc., New York, 1932) 2nd ed. p. 249.

is seen that they are independent of the frequency between 10 to 10^5 kc/sec, but an increase is observed in the lower frequency range.

Fig. 7 shows the temperature dependence of the dielectric constants of ammonium sulfate in three axial directions at 1440 kc/sec. One can see two following characteristic points.

First, the anomaly characterized by a sharp peak in dielectric constant is seen in the direction of *a*-axis of the crystal (applied electric field being parallel to *a*-axis), and in two other directions kinks are observed at the same temperature. These results resemble those of KH_2PO_4, in which, according to the measurement of Busch[10], *c*-axis has a peak and *a*-axis has a kink.

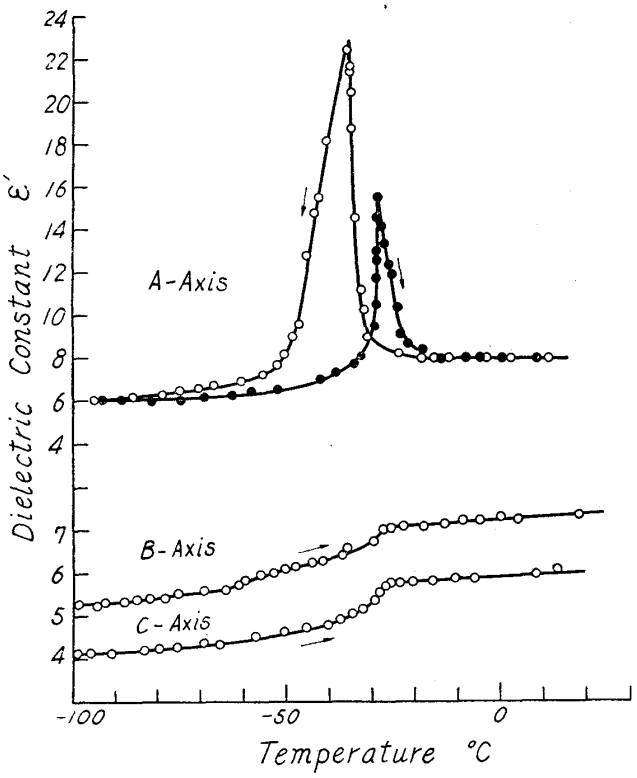

Fig. 7. Temperature dependence of the dielectric constant in three axial directions of ammonium sulfate at 1440 kc/sec.

The second characteristic point is its transition temperature, which is −36°C on cooling and −29°C on warming. These temperatures are much higher than those (about −50 °C) observed by Guillien, Freymann and others who used crystalline powder specimens. They are still higher as compared with the results by Bayley and Hettner and Simon. The transition temperature is, in general, considerably affected by the rate of cooling or warming, in this experiment the rate being about 10°C per hour. For a little rapid rate of change in temperature, the transition temperature at about −9°C was observed on warming, the result of which is shown in Fig. 8. The frequency is 1 kc/sec in this experiment.

It should be noted that in the single crystal specimen the transition, once it begins, has a tendency to keep on going automatically in spite of temperature being kept constant. Therefore the peak in dielectric constant is very sharp and nearly perpendicular to abscissa, as seen in the ascending part of the peak in Fig. 7.

For comparison with the results made by other workers, measurements were made with the crystalline powder specimen. The results are shown in Fig. 9. Specimen was made by pressing machine, porosity being 0.877. The frequency used was 2 mc/sec. The transition temperature is −52.5°C, which is quite close

(10) G. Busch, Helv. Phys. Acta **11** (1938), 269.

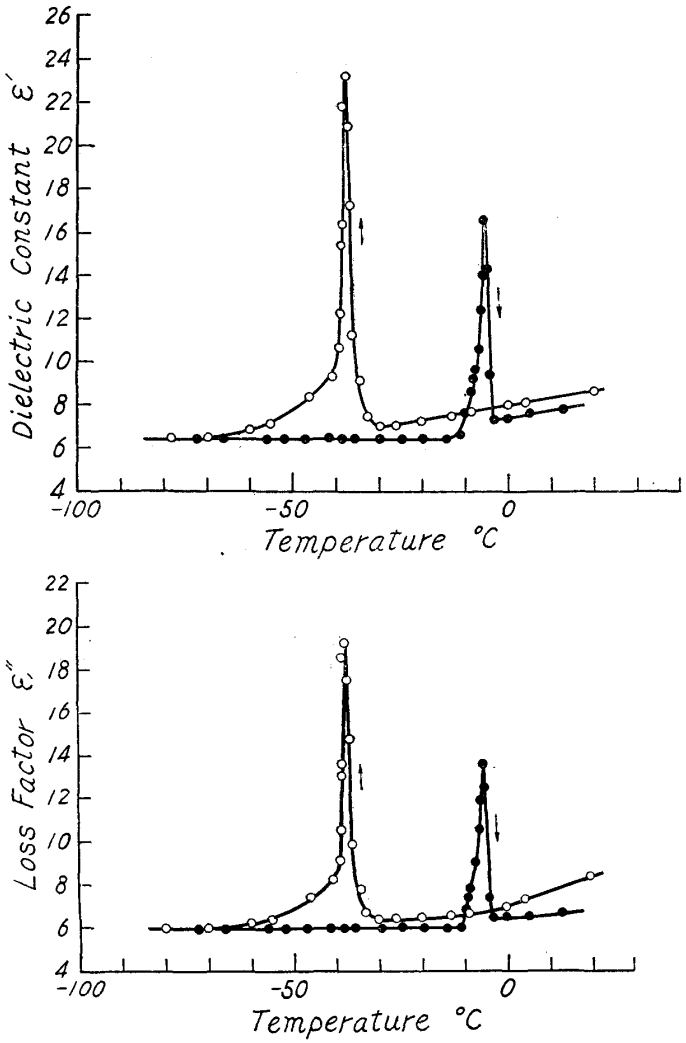

Fig. 8. Temperature dependence of dielectric constant and loss factor in *a*-axial direction of ammonium sulfate at 1 kc/sec.

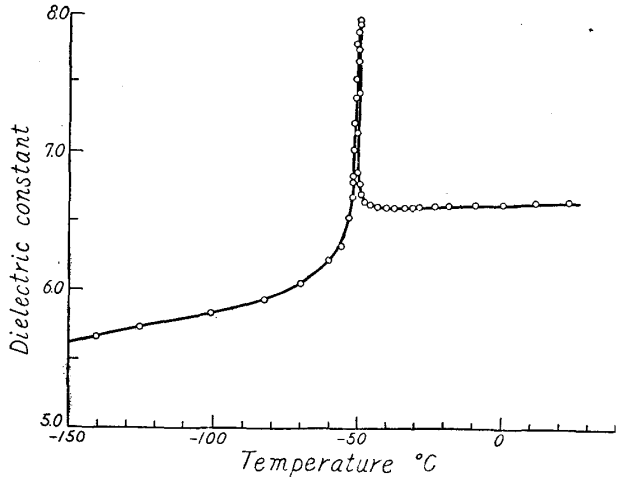

Fig. 9. Crystalline powder sample. Porosity : 0.877, frequency : 2 mc/sec. Rate of cooling : 3°C/hour between −50 and −55°C and 13°C for other temperature range.

to those observed by Guillien[4] and Freymann[5] who used the crystalline powder specimen. Fig. 9 also shows that the peak is very sharp when the temperature control is adequate. The rate of cooling in this experiment is 3°C per hour between −50°C and −55°C and about 13°C per hour for other temperature range. The width of the peak is about 1°C. Fig. 10 is also the results obtained by the crystalline powder sample. But its porosity is much smaller (about 0.56), and measurements were made at two different rates of cooling. The transition temperature was found to be about −50°C on slow cooling (15°C/hour) and delayed to as low as −80°C on rapid cooling (50°C/hour).

It is seen from Figs. 9 and 10 that the transition temperature of the crystalline powder specimen is not affected by the change in apparent density or porosity. It will be seen in Fig. 11 that the transition temperature is not affected even when the porosity is 0.961, which is nearly equal to that of a perfect crystal. They do not have the tendency to shift from about −50°C to −36°C which was observed in the single crystal specimen. Therefore, it can be said that the transition phenomenon is delayed on cooling when the specimen is polycrystalline form, but the reverse is true on

warming, or, in other word, that the low temperature state of single crystal is more stable than that of polycrystalline powder.

Fig. 11 shows the effect of humidity on the transition temperature of ammonium sulfate, that is, measurements were made at 100 kc/sec at the same cooling rate on the same specimen before and after it is dried. The specimen is a pressed disk, porosity being 0.961. In this figure curve "*a*" represents the result obtained by the specimen before drying; the dielectric constant at room temperature is very large because of condtctivity, and the transition temperature is about −65°C. After thorough drying (curve "*b*" in the figure) the transition temperature shifts to −52.5°C, which in the same temperature as that shown in Fig. 9. Therefore, the transition temperature is, to some extent, hindered by the presence of humidity in the specimen, which is contrary to the results obtained by Stephenson *et al*[11] on the transition temperature of ammonium iodide. They observed that the transition of NH_4I is hindered by thorough drying.

The dielectric constant at the peak changes considerably if the alternating electric field is continuously applied. This is shown in Fig. 12, where abscissa represents the time during which the measuring field is applied and the ordinate the dielectric constant. The dielectric constant decreases with time and tends to a certain value, the amount of decrease is larger for higher frequency.

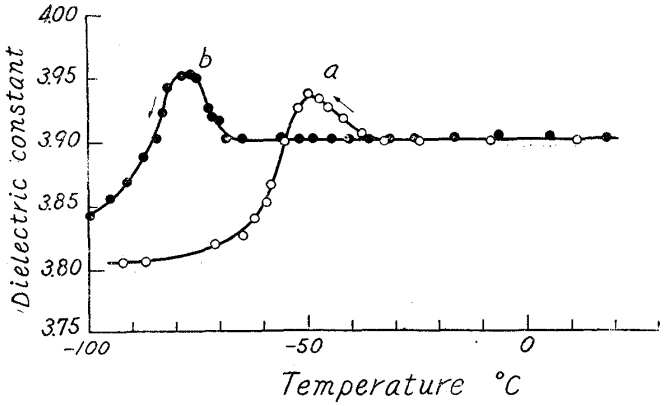

Fig. 10. Crystalline powder sample. Porosity : 0.56, frequency : 1440 kc/sec. Curve "*a*" : slow cooling (15°C/hour), curve "*b*" : rapid cooling (50°C/hour).

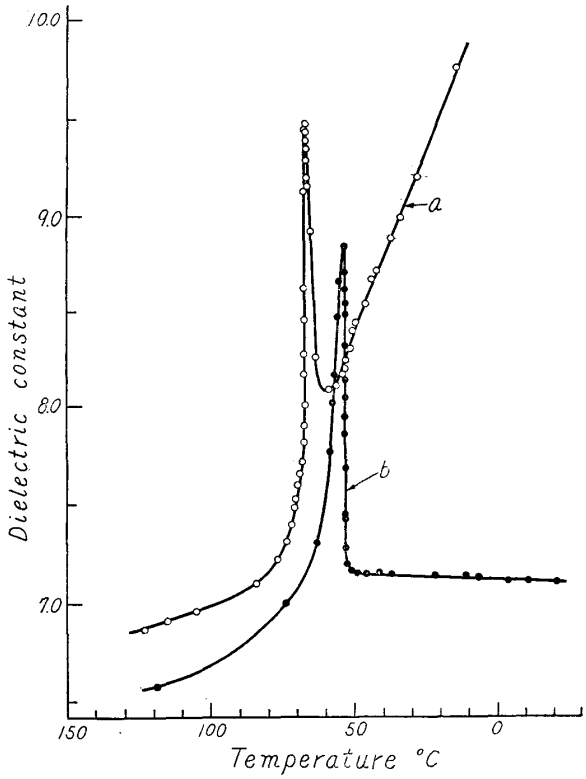

Fig. 11. Effect of humidity content in the sample on the transition temperature. Frequency : 100 kc/sec. Crystalline powder sample of porosity 0.961. Curve "*a*" : before drying, curve "*b*" : after drying.

(11) C. C. Stephenson, L. A. Landers and A. G. Cole, J. Chem. Phys. **20** (1952), 1044.

No anomaly is observed in ammonium sulfate in the temperature range from room temperature up to about 200°C (see Fig. 13).

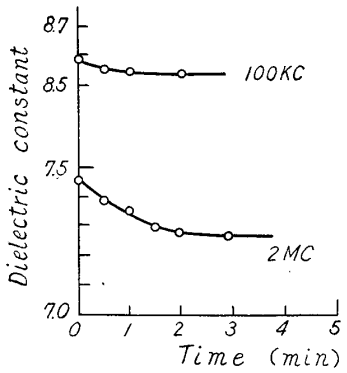

Fig. 12. Change of the dielectric constantat at the peak with the time during which the high frequency field is continuously applied.

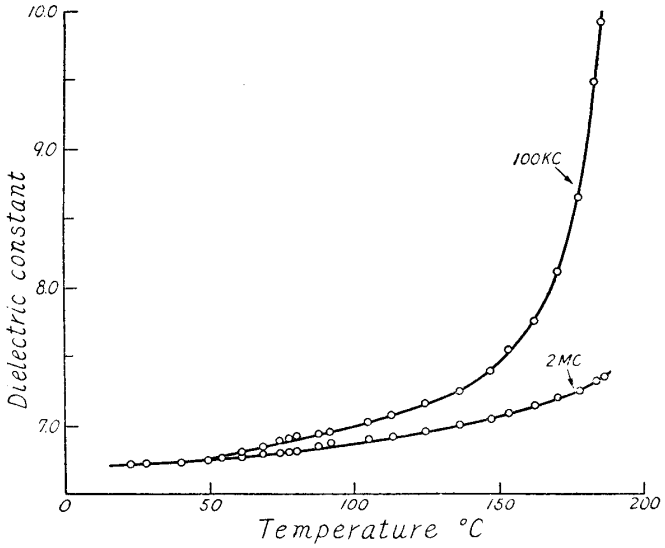

Fig. 13. Variation of the dielectric constant of ammonium sulfate at high temperature. Crystalline powder sample, porosity : 0.877.

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